

THE FLOTATION CHEMISTRY OF NONSULFIDE MINERALS

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Introduction

The dimensions of nonsulfide flotation technology extend in many different directions, as might be expected from the diversity of the mineral classes, which include soluble salt minerals (potash, borax, and trona), semi-soluble salt minerals (phosphate minerals, fluorite, calcite, and barite), insoluble oxides/silicate minerals (iron oxide minerals, rutile, mica, quartz, and feldspar), and energy minerals (coal and oil sands). As a consequence, some flotation separations are accomplished from saturated brine, while other separations are achieved in solutions of rather low ionic strength. Also it is worth noting that certain nonsulfide minerals are naturally hydrophobic, such as talc, graphite, and coal. But in general, the nonsulfide minerals are hydrophilic and require relatively high levels of collector addition on the order of 1 lb/ton to establish a hydrophobic surface state. Further, the nonsulfide collectors generally are anionic or cationic surfactants, having hydrocarbon chains often carbon atoms or greater. In many instances, the collector is sufficiently insoluble that a distinct collector phase is present in the system, existing as a dispersion or as a collector colloid. This situation further complicates the analysis of nonsulfide flotation chemistry, and in view of the foregoing, it is evident that the flotation chemistry is distinctly different from the flotation chemistry of sulfide minerals.

Nonsulfide flotation technology also differs from sulfide flotation technology with respect to particle size. In many nonsulfide systems, but not all, flotation is accomplished with deslimed feed and a particle size that extends up to several millimeters in diameter (coal, phosphate, and potash). On the other hand, some nonsulfide flotation systems involve flotation of micron-size particles (taconite and kaolin).

With respect to flotation rate, again, the variation is great, with long retention times (even one hour) required for the flotation of impurities (anatase, etc.) from kaolin, whereas rather rapid flotation (a few minutes of retention time) is required for phosphate flotation.

Advances in nonsulfide flotation, have been documented in Section 3 of the Proceedings, Advances in Flotation Technology, a recent conference in honor of Professor M. C. Fuerstenau [1].

One important aspect of the flotation technology for nonsulfide minerals is the matter of flotation chemistry, and in this regard creation of the hydrophobic surface state for selected nonsulfide flotation systems is discussed. Because of space limitations only semi-soluble salt flotation systems are examined taking into consideration the fact that in some cases the hydrophobic surface state is created by the adsorption of water-soluble collector species while in other cases the hydrophobic surface state is created by the wetting/spreading of insoluble collector oils or by the attachment of insoluble collector colloids.

Numerous semi-soluble salt minerals are recovered by flotation (phosphate minerals, fluorite, calcite, and barite). In many cases the hydrophobic surface state is created by adsorption of water-soluble collector species. Most frequently anionic collectors such as carboxylates and sulfonates are used. The hydrophobic surface state is generally established by chemisorption and/or surface precipitation reactions. Probably the most studied and the best understood system is the fluorite/oleate system. Rather detailed quantitative information regarding adsorption phenomena has been obtained by various experimental techniques. Most recently the in-situ FTIR/IRS technique has further extended our understanding of adsorption phenomena and the state of the adsorbed collector.

Adsorption Phenomena

In general the oleate adsorption isotherms presented in Figure 1 are characterized by at least two regions. At low equilibrium oleate concentrations ($< 1 \times 10^{-5}$ M), in the absence of calcium dioleate precipitation, the density of the calcium surface sites (Table 1) dictates the adsorption density in this plateau region for the endothermic chemisorption reaction [2]. In the case of fluorite, the adsorption density plateau for adsorbed oleate is 6.5 to 6.8 $\mu\text{mole/m}^2$ such as would be expected for a close-packed monolayer. Taking into consideration the density of calcium sites, this corresponds to a calcium-to-carboxylate ratio of about 2 to 1 and suggests that bridging occurs between a carboxylate group and two calcium ions at the fluorite surface. See Figure 2. Such coordination appears to explain the spectral features of the chemisorbed carboxylate group [3]. On the other hand, the chemisorption "plateau" for calcite and apatite as determined from Figure 1 at low equilibrium oleate concentrations is significantly less, approximately 1 to 2 $\mu\text{mole/m}^2$. Clearly a close-packed monolayer is not achieved for calcite and apatite at low concentrations, which accounts for a diminished state of hydrophobicity under these

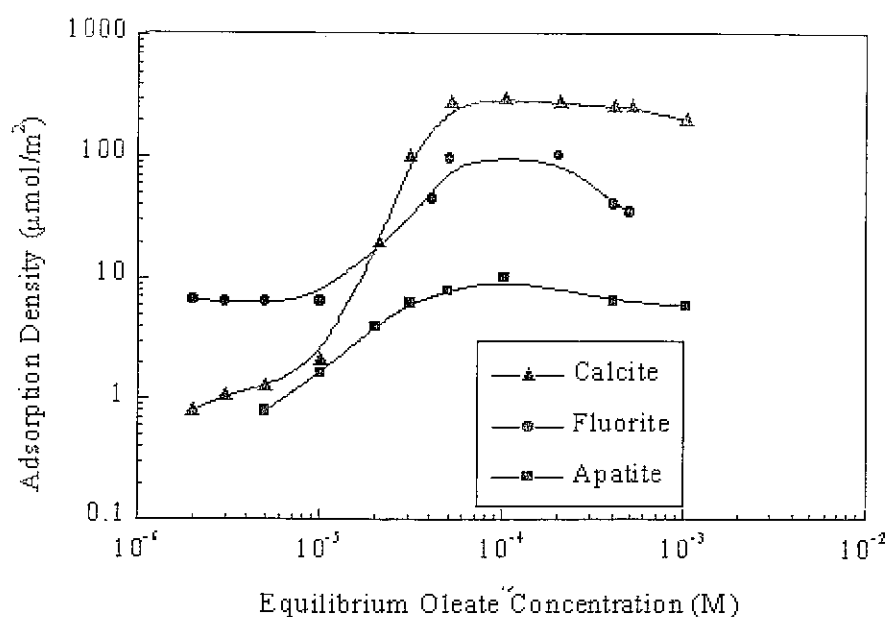


Figure 1. Comparison of oleate adsorption isotherms at apatite, fluorite, and calcite surfaces at about pH 9.5 and a temperature of 20°C to 25°C [2].

Table 1. Significance of Calcium Surface Site Density in Oleate Adsorption for Selected Semi-Soluble Salt Minerals [2]

Surface	Calcium Surface Site Density (μmole/m ²)	Adsorption Density from 1×10 ⁻⁵ M Oleate Solution (μmole/m ²)
Fluorite (111)	12.9	6.5-6.7
Calcite (111̄)	8.24	2.5-3.2
Apatite (0001)	6.57	1.5-2.0

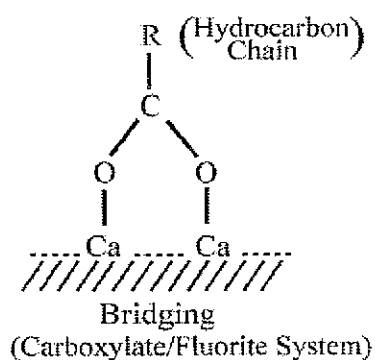


Figure 2. The bridging coordination believed to define the nature of carboxylate chemisorption at the fluorite surface [3].

circumstances when compared to fluorite. For example, it has been found that for a 1×10^{-5} M equilibrium oleate concentration, fluorite exhibits a contact angle of close to 90° , whereas bubble attachment at a calcite surface does not occur [4].

In region two at higher equilibrium oleate concentrations ($>1 \times 10^{-4}$ M) where adsorption exceeds an effective close-packed monolayer, the maximum adsorption densities are found to be about $300 \mu\text{mol/m}^2$ at a calcite surface, $100 \mu\text{mol/m}^2$ at a fluorite surface, and only $11 \mu\text{mol/m}^2$ at an apatite surface. In this region it appears that the adsorption is mainly due to surface precipitation of calcium dioleate or heterocoagulation (attachment) of calcium dioleate collector colloids. Therefore, it is reasonable to relate adsorption density to the extent and kinetics of calcium ion release to solution as has been discussed in the literature [4, 5]. In this regard, it should be noted that the adsorption isotherm is quite sensitive to the level of dissolved calcium, particularly region one, the chemisorbed layer. If even a modest amount of calcium is present in solution prior to oleate addition, the precipitation event can overwhelm chemisorption and the plateau, so characteristic of the chemisorbed monolayer, can be eliminated as demonstrated for the fluorite system by Free and Miller [5].

The significance of mineral composition is revealed in oleate adsorption studies for different apatites as shown in Table 2 [6].

Table 2. Comparison of Adsorption Density, Contact Angle, and Flotation Recovery for Apatite Minerals with Oleate as Collector at 5×10^{-4} M and pH 10 [6].

Apatite Mineral	Adsorption Density, mg/m^2	Surface Coverage	Contact Angle, degrees	Flotation Recovery, %
Fluorapatite	1.08	0.49	55	88.7
Carbonatapatite	0.86	0.39	43	71.3
Hydroxylapatite	0.52	0.24	38	62.5
Chlorapatite	0.34	0.20	No Attachment	53.2

Sensitivity of the adsorption reaction and the hydrophobic surface state to apatite composition is clearly revealed from the data. Greater hydrophobicity is obtained for the fluorapatite, which appears to account for the activation of francolite phosphate minerals which can be achieved with the addition of sodium fluoride [7].

The two regions of oleate adsorption (chemisorption and surface precipitation) are also revealed from thermochemistry studies of the fluorite/oleate system [8] and for the calcite/oleate system [4]. As shown in Table 3, adsorption at low equilibrium oleate concentrations reveals an endothermic reaction of oleate at the fluorite surface, whereas at high equilibrium oleate concentrations an exothermic reaction associated with multilayer adsorption by surface precipitation of calcium dioleate is observed.

Table 3. Comparison of the Measured Heats of Adsorption of Oleate at the Fluorite/Water Interface with Isosteric Heats of Adsorption for Different Levels of Surface Coverage [8]

	Heats of adsorption of oleate (kcal mol^{-1})	
	Measured by Microcalorimetry	Calculated from Adsorption Isotherm Data
Chemisorption (monolayer coverage)	2.36	2.77
Surface Precipitation (above monolayer coverage)	-5.31*	-6.60

*At oleate surface coverage $\theta_2 = 0.59$ (i.e., $\theta = 1.59$).

The organization of carboxylates at the fluorite surface has been studied by in-situ FTIR/IRS technique [9] and the results show that spontaneous adsorption of oleate or stearate from solution results in a self-assembled chemisorbed monolayer almost identical to the structure of transferred LB films as shown in Table 4. These results again support bridging of the chemisorbed oleate as shown in Figure 2.

Table 4. Contact Angle Data for Transferred LB and SA Stearate Monolayers at a Fluorite Surface (Drop Size Varied from 2 to 6.5 mm, pH 5.8) [9]

Monolayer Type	Adsorption Density ($\times 10^{-10}$ mol/cm ²)	Molecular Orientation Angle (degrees)	Advancing Contact Angle (degrees)	Receding Contact Angle (degrees)
LB	8.1	13	110-114	98-102
SA	7.6	21	110-115	75-85

In summary, based on these adsorption density and thermochemistry considerations, chemisorption predominates at low equilibrium concentrations (low adsorption densities) and a precipitated calcium dioleate predominates at higher equilibrium concentrations. In the case of fluorite, a close-packed monolayer of oleate forms during the chemisorption reaction, creating a strong hydrophobic state at the fluorite surface. On the other hand, in the case of calcite and apatite, monolayer formation is incomplete during chemisorption in region one, and, at best, a weak hydrophobic state is created at these surfaces.

Insoluble Collectors.

It is evident from the foregoing that the solubility limit of long-chain carboxylate collectors can be exceeded, and under these circumstances another phase appears in the system, either a collector oil (oleic acid) or a collector colloid (calcium dioleate). Under such conditions the hydrophobic surface state may be created by the attachment of this new collector phase at the surface [10]. For example, such phenomena have been discussed in the literature for semi-soluble salt minerals including fluorite [11]. These results suggest that the interaction of calcium dioleate collector colloids at the fluorite surface can be quite strong, leading to a very hydrophobic surface.

This expectation is revealed by flotation recovery curves for fluorite and calcite with calcium dioleate as collector [12]. As shown in Figure 3, flotation of fluorite is quite strong with the calcium dioleate collector colloid, whereas such is not the case for calcite. The tendency for attachment of the calcium dioleate collector colloid at fluorite and calcite surfaces is revealed from AFM force/distance diagrams using a 14-micron calcium dioleate sphere as the colloidal probe. See Figure 4. Significant attraction in the case of fluorite is evident. Furthermore, if the fluorite has a chemisorbed monolayer of oleate, the attractive force between calcium dioleate and the surface is so strong that measurement is difficult with standard cantilevers.

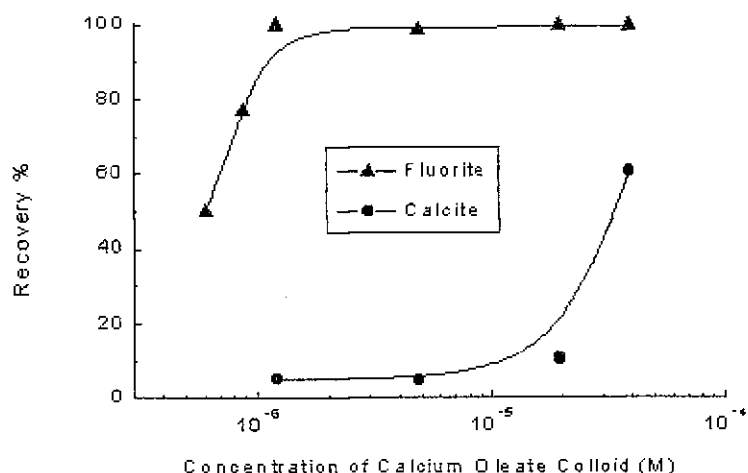


Figure 3. Comparison of the microflotation response of fluorite and calcite as a function of calcium dioleate collector colloid concentration [12].

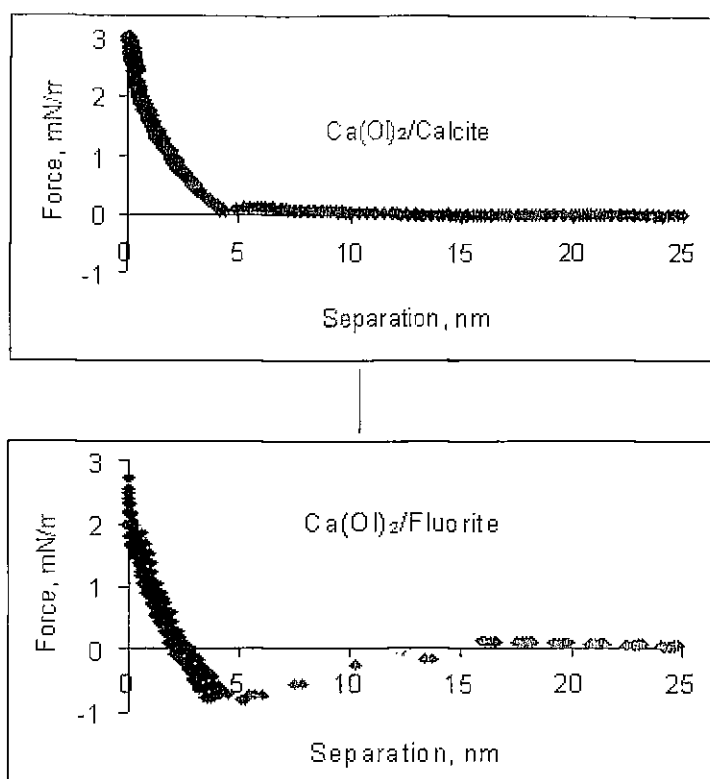


Figure 4. AFM force/distance curves between calcium dioleate sphere and calcite, fluorite surfaces at pH 8.1 and 25°C [12].

Probably of greater commercial significance is the flotation chemistry associated with phosphate rock. The chemistry fundamentals of fatty acid flotation of phosphate minerals have been studied extensively, and this research provides a basis for the understanding of industrial practice. However, there is still much unknown regarding the collector adsorption and oil wetting phenomena which occur in the actual flotation of phosphate rock at plant operations. Important issues include water quality as well as structure and composition of phosphate minerals.

However, it is generally recognized in plant operations that flotation of the francolite phosphate mineral is not effective without the use of an insoluble collector oil, a mixture of fatty acid and fuel oil which selectively wets the phosphate mineral surface during high solid conditioning. At a critical coverage of the oil, aggregation of the wetted phosphate mineral particles occurs with the formation of dense aeroflocs which are separated into the multiphase froth. As shown from the 3D x-ray micro CT image in Figure 5, the structure of the froth is rather complex, with not only mineral particles, water, and air bubbles, but also the oil phase [13].

Of particular importance in the case of coarse particle flotation with insoluble collector oils is the distribution of the oily collector to facilitate selective wetting/spreading at the mineral surface, a phenomenon which is of importance not only to the phosphate industry but also to the coal and potash industries. In this regard dispersion of the oily collector (high solids conditioning with a fatty acid/fuel oil mixture for phosphate rock) is an important factor as discussed and demonstrated in several studies [14,15]. In the case of phosphate flotation, it has been shown that the use of certain nonionic surfactants facilitates the flotation of coarse phosphate due in part to the improved dispersion of the fatty acid/fuel oil mixture. See Figure 6.

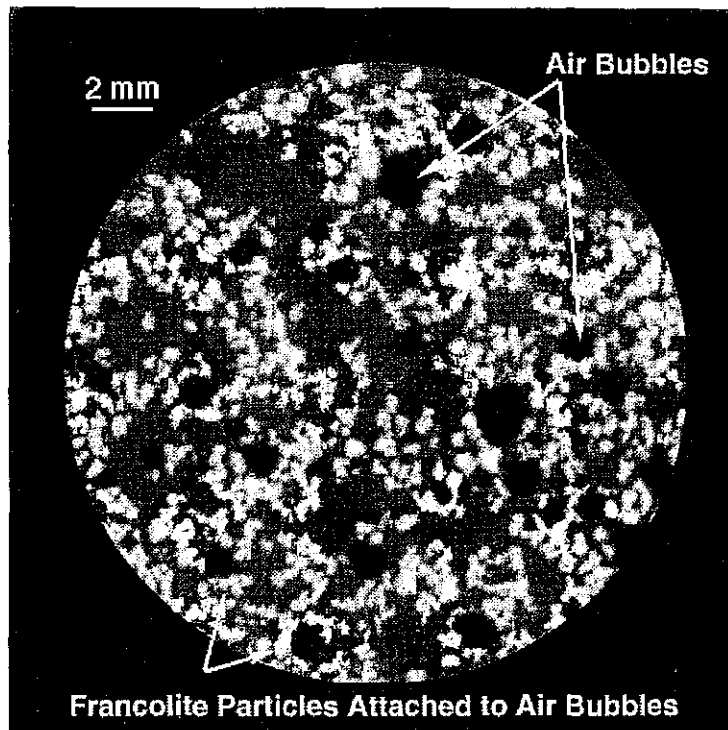


Figure 5. Section of a 3D x-ray micro CT image of the dense aerofloc structure of a phosphate concentrate [13].

Recent research relates the improved flotation with high solids conditioning to the selective wetting of phosphate minerals by the fatty acid/fuel oil mixture [16]. Results from an experimental study with a high-speed video system clearly show the preferential transfer of oil to a francolite surface (carbonate fluorapatite) and helps to explain the high solids conditioning mechanism. When a quartz particle with an attached oil drop interacts with a francolite particle, the oil drop will spread at the francolite interface. When these two particles are forced apart, a major portion of the oil drop is transferred to the francolite surface. See Figure 7. A small portion of the oil drop may remain at the quartz surface. This process happens

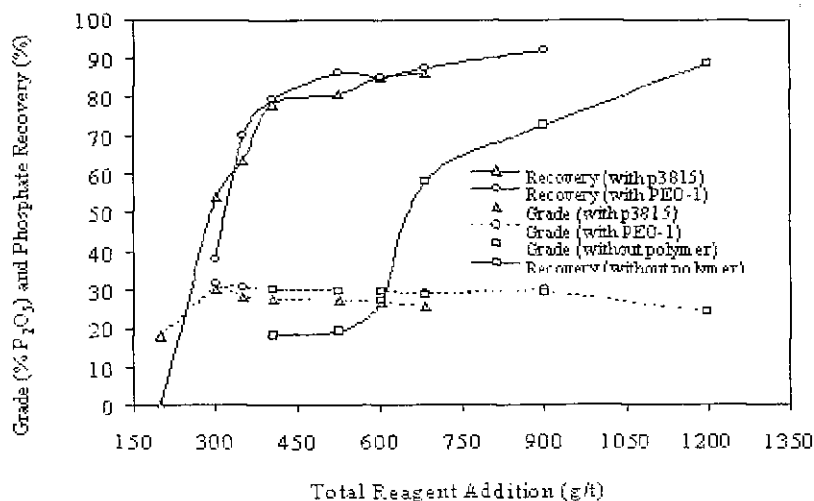


Figure 6. Effect of reagent type and dosage on phosphate grade and recovery, coarse feed, 10% polymer, fatty acid/fuel oil 7:3, pH 9 [14].

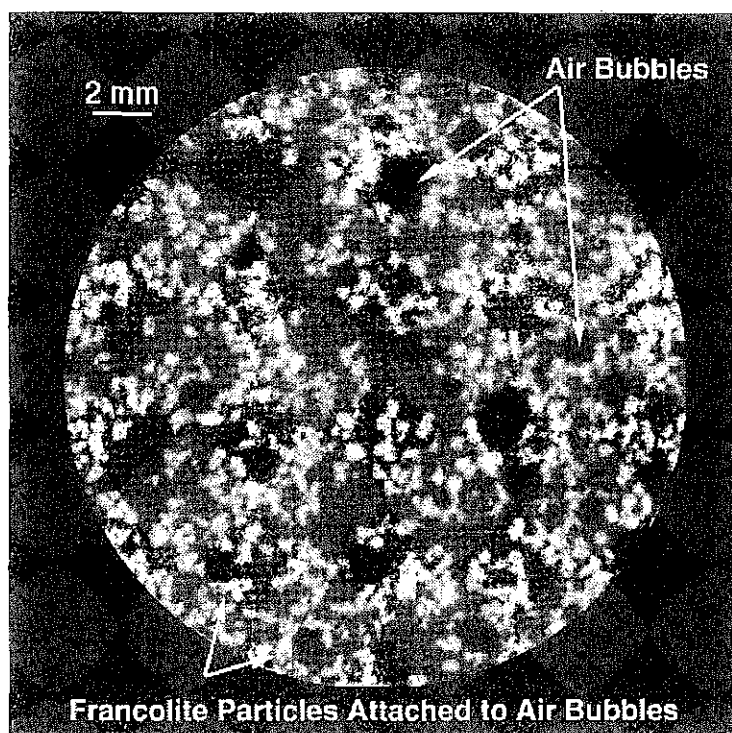


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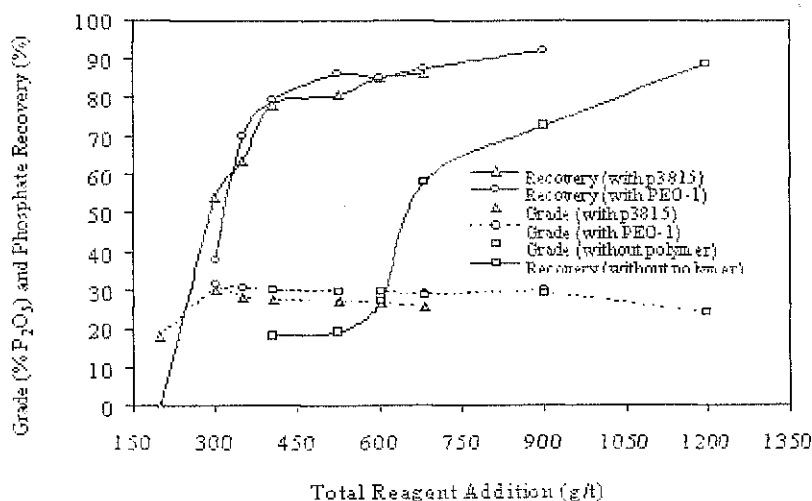


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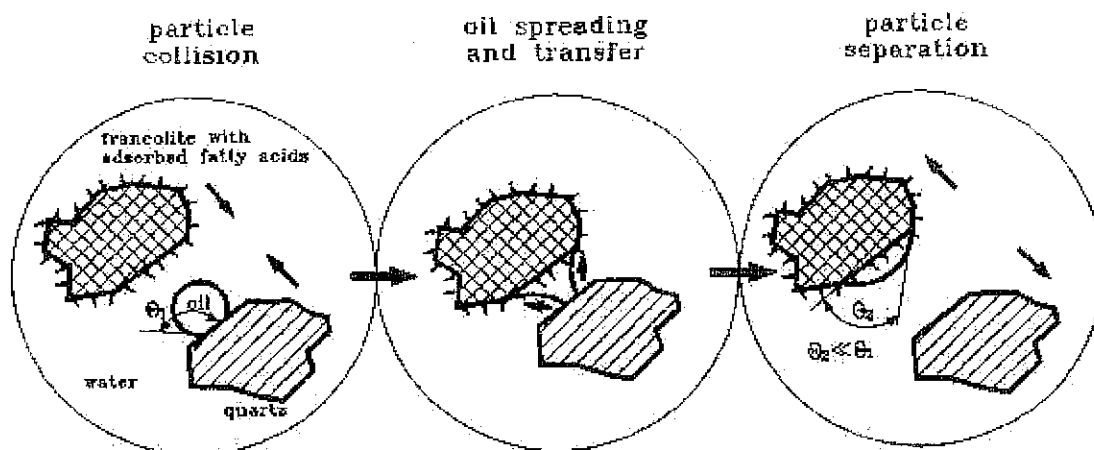


Figure 7. A simplified interpretation of phenomena involved for the oil transfer from quartz particles to francolite particles during the high solid conditioning of phosphate rock with fatty acid and fuel oil [16].

again and again during high solids conditioning, and the fatty acid/fuel oil collector which initially may be randomly distributed will ultimately be transferred to the surfaces of francolite particles. In this way, flotation selectivity is improved. Therefore, both recovery and selectivity in phosphate flotation with fatty acid/fuel oil are improved by high solids conditioning.

Summary

For certain nonsulfide mineral systems, oxides/silicates and semi-soluble salts, collector adsorption phenomena has been studied in considerable detail and related to the hydrophobic surface state. For example in the case of semi-soluble salt minerals conditions for which a well ordered chemisorbed monolayer of oleate is achieved by self assembly have been identified for the fluorite/oleate system. At higher oleate and/or calcium ion concentrations, multilayers of a calcium oleate surface precipitate or collector colloid accumulate to establish the hydrophobic surface state. Further research is warranted particularly with regard to the spatial organization of collector molecules at the surface of nonsulfide minerals. Also study of collector adsorption by soluble salt minerals in the absence of precipitation reactions is needed to identify the nature of the adsorbed state as influenced by brine composition.

In addition to the adsorption of water soluble collector species, attention must now be given to the use of water insoluble collector colloids/oils and the attachment/wetting phenomena that allows for selective flotation separations. Frequently these systems involve the use of hydrocarbon oil and are intrinsically more complicated since there is another phase to take into consideration...Does the collector completely wet the surface? Is the collector phase uniformly distributed at the surface of the nonsulfide mineral? What is the thickness of the film? Is an ionizable collector required, eg. fatty acid in the case of phosphate flotation, to achieve spreading of the oil? If so, how is the ionizable collector distributed between the aqueous and organic phases? It is evident that many research challenges in nonsulfide flotation chemistry remain to be solved for development of more efficient flotation separations. With advanced instrumentation it seems that many of these flotation chemistry issues associated with nonsulfide flotation systems can now be understood in greater detail.

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